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The Velocity of Saponification of Fats and Oils by Potassium Hydroxide in Different Solvents

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THE VELOCITY OF SAPONIFICATION OF FATS AND OILS BY POTASSIUM HYDROXIDE IN DIFFERENT SOLVENTS

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By

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The Velocity of Saponification of Fats and Oils by Potassium Hydroxide in Different Solvents.

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The Purpose of the Investigation.

The purpose of the investigation was to determine the influence of certain factors on the velocity of saponification of fats and oils by potassium hydroxide.

The idea of measuring the velocity of a reaction was first suggested by K. F. Wenzel[1] in 1777. Wenzel defined the velocity of a reaction as the ratio, $\left(\frac{dx}{dt}\right)$ of the amount of substance changed to the time in which it is changed. This definition is still accepted.

The factors influencing the velocity of a reaction are, in general, the concentration of the reacting substances, the temperature, the pressure, the solvent, catalytic agents, and the homogenity or heterogenity of the system. Of these, the factors that need to be considered in this work are:

(a) Concentration of reacting substances

(b) Temperature

(c) Solvent

(d) Catalytic agents.

The influence of concentration on the velocity of reaction is best stated by the law of mass action; the velocity

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1. Wenzel: Lehre von der Verwandtschaft de Körper. 1800

of a reaction is directly proportional to the concentration of the reacting substances.

The velocity of reactions is in general increased by a rise in temperature. Vant Hoff has shown that a rise of ten degrees doubles or trebles the velocity of reaction. However it has recently been shown that the velocity of some reactions is decreased by a rise in temperature.

The influence of the solvent on the velocity is very great as shown by Menschutken[2]. The change in velocity due to the change of solvent is connected with the displacement of the equilibrium. On the whole, therefore, the change in velocity may be divided into two parts, one of which acting equally on the two reciprocal reactions, may be compared with catalytic action and may depend upon any of the physical properties of the solvent. The other part, acting differently on the reciprocal reactions must be of a specific nature, and be connected with some interaction between the solvent and the reacting bodies.

The velocity of reactions is very greatly changed by the presence of traces of some substances which do not appear to enter into the reaction. This phenomenon is spoken of as catalysis. In some cases the velocity of the reaction is increased as in the inversion of cane sugar by traces of strong acids. In other cases the velocity of the reaction is decreased. When one of the reaction products acts catalytically

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2. Z. f. Phys. Chem. 6, 41-57.

on the reaction the phenomenon is spoken of as auto-catalysis. The characteristic course of a reaction involving auto-catalysis is small at first, ascending to a maximum and then descending. Closely connected with catalysis is the effect of moisture on the velocity of chemical reactions.

Reactions are classified as monomolecular, bimolecular, etc., according to the number of molecules entering into the reaction and these classes are known technically as "first order", "second order" etc. To each order corresponds a definite mathematical formula. Velocity data substituted in these formulas give a constant value with only one formula. This enables us to determine the order of any chemical reaction.

Previous Work Bearing on the Velocity of Saponification Reactions.

Geitel[3] first showed that the reaction underlying hydrolysis is primarily bimolecular. The term saponification is generally applied to those chemical reactions in which hydrolysis is brought about in the presence of an alkali, a salt and an alcohol being the final products.

There has been much controversy as to the exact reactions which take place during the saponification of glycerides. The theory usually accepted is that the alkali acts as an accelerating agent and that no saponification can take place in the absence of water. However Bois[4] carried on experiments

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3. Jour. F. Pract. Chem. 35, 429. (1877).
4. Compt. rend. 45, 35.

with sodium ethoxide that purported to show that saponification will take place in the absence of water. Kremann[5] makes the statement that the saponification of ethyl acetate is 1000 times as fast in an aqueous solution as it is in absolute alcohol solution. Klimont[6] in 1901 showed that a glyceride can be hydrolysed by water alone under a pressure of 15 atmospheres, equivalent to a temperature of 220°C.

Some investigators hold that hydrolysis takes place in three steps, others that it takes place in one step. Lewkowitsch[7] believes that the reaction proceeds in steps but does not claim that the whole mass of triglyceride is first hydrolysed exclusively to diglyceride and so on down to glycerol but rather that three steps take place concurrently. Lewkowitsch has attempted to prove his views by the large variations of the acetyl values at different intervals during the reactions. Marcusson[8] rejects the theory of Lewkowitsch and endeavors to show that the high acetyl values are due to the accumulation of water soluble acids and to oxygen absorption from the air.

This hydrolysis, however it takes place, may be accelerated by an acid, an alkali or a ferment. Of these three agents, an alkali is usually employed.

If an alkali does act as a catalytic agent, the alkali

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5. Kremann: The Application of Physico-Chemical Theory to Technical Processes.
6. Z. f. angew Chem. (1901) 127.
7. A. Chem. Jour. 45
8. Rev. Fett Harz. Ind. 15, 255.

need not be present in molecular proportions. This has been proven to be true. Lewkowitsch has found that where a certain glyceride would under ordinary conditions actually require 14 per cent of lime, under a pressure of 12 atmospheres even one per cent of lime was sufficient for complete hydrolysis.

Usually, less soluble material such as oxides of zinc, magnesium, calcium, barium, and lead, even when used in excess do not give so complete saponification as either sodium or potassium hydroxide. In the saponification of glycerides, potassium hydroxide is generally used in preference to sodium hydroxide because of the greater solubility of the potassium salts of the fatty acids usually met with in oils and fats. There is not however much difference in the saponifying power of the two hydroxides.

Acree[9] and Shidinger found that the change of alkali from potassium to sodium hydroxide had very little effect upon the saponification velocity of alkyl halides.

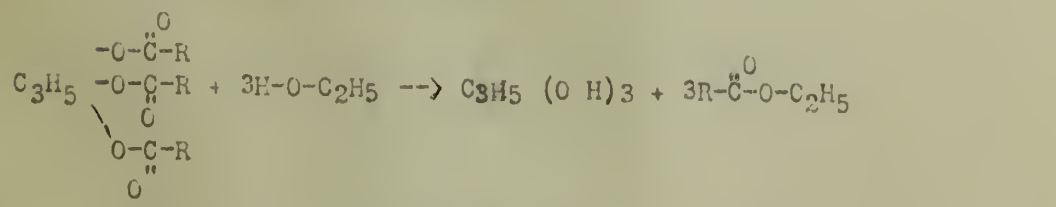
Reicher[10], by saponifying methyl acetate at 9.4° by various bases obtained the following results.

Base	Constant
Na O H	2.307
K O H	2.298
$Ca(OH)_2$	2.285
$Sr(OH)_2$	2.204
$Ba(OH)_2$	2.144
NH_4OH	0.011

9. Am. Chem. Jour. 39, 255
10. Z. f. Phy. Chem. I, 110, (1887).

When saponification is brought about by boiling a glyceride with the theoretical amount of any alkali the reaction is not complete. Clapham[11] found that only 94 per cent of tallow was saponified by the theoretical amount of sodium hydroxide.

The reaction which takes place when alcoholic alkali is used does not differ from hydrolysis in aqueous solution, if alcohol is looked upon as water with one hydrogen replaced by an alkyl radical.



Fat + alcohol --> glycerol + ester.

In the absence of water, the above reaction could not go beyond the formation of the ester if the results of Henriques[12] and Kruger[13] are conclusive. Henriques demonstrated that if an insufficient amount of alkali is used, the chemical change taking place consists in the complete splitting off of glycerol with the formation of ester.

Other solvents than alcohol also change the velocity of saponification. Yssel de Schepper and Geiter and Hehner add a small amount of ether to the reaction mixture. Henriques dissolves the fat in petroleum ether.

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11. Lewkowitsch; Oils, Fats and Waxes. (1914 Ed.) 52.
12. Jour. Soc. Chem. Ind. (1892) 673.
13. Z. f. Phys. Chem. 15, 32. (1891).

Dean[14] after studying the velocity of saponification of the esters of substituted acetic and propionic acids by sodium hydroxide, drew the conclusion that the velocity is largely a function of the strength of the acid from which the ester is derived.

Reichert found that, as a whole, the more atoms present in the ester saponified, the smaller was the reaction velocity. The following table taken from his work illustrates this point.

Ethyl Acetate	3.204
" Propionate	2.186
" Butyrate	1.702
" Iso-butyrate	1.731
" Iso valuate	0.614
" Benzoate	0.830
Methyl Acetate	3.492
Ethyl "	2.307
Propyl "	1.92
Iso Butyl "	1.618
Iso Amyl "	1.645

Since the saponification of a glyceride by alcoholic K O H, is supposed to take place through the hydrolysis of the ester, it would seem that the velocity of saponification of glycerides should also depend upon the strength of the fatty

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14. Am. Jour. Sci. 35, 605.

acids involved or upon the number of atoms present in the ester. On the other hand Henriques[15] has found that on saponifying glycerides with amounts of caustic alkali insufficient to neutralize all the fatty acids formed no difference in the speed of saponification of the several glycerides could be observed.

Various investigators hold different opinions as to the order of saponification. All agree that such reactions as that between ethyl acetate and aqueous potassium hydroxide are bimolecular. In the saponification of glycerides there seem to be two orders which the reaction may follow. When the saponifying agent is in excess the reaction is monomolecular, when the saponifying agent is present in moderate amounts the reaction is bimolecular. Kellner[16] has found however that when palm kernel oil is hydrolysed by an alkali hydroxide under atmospheric pressure, the reaction is tetra molecular, and no bi- or monoglycerides are formed as intermediate products.

Method of Procedure.

There are two or three different methods by which the velocity of saponification may be determined. In this investigation the valumetric method was used. It is very accurate though possibly not so accurate as the conductivity method as carried out by Walker,[17] Stieglitz[18] and Derby.

The exact procedure followed in this investigation is given below. A certain volume of oil, usually five or ten cubic

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15. Jour. Soc. Chem. Ind. (1898) 673.
16. Jour. Chem. Soc. (London) 96, 357 (1909).
17. Chem. News. 94, 238.
18. Am. Chem. Jour. 31, 449.

centimeters was made up to 100 cubic centimeters with the desired solvent and placed in the thermostat. At the same time an equal volume of potassium hydroxide in the same solvent was placed in the thermostat. After the two solutions had reached constant temperature, they were mixed. At suitable intervals which depend upon the velocity of the particular reaction ten cubic centimeters of the reaction mixture were withdrawn and run into an excess of N/10 hydrochloric acid, the time being accurately noted. The excess hydrochloric acid is then titrated with N/10 barium hydroxide using phenolphthalein as indicator. This titration was made in 50 cubic centimeters of ethyl alcohol so that the final mixture would in all cases be clear, thus making possible a delicate end point.

The Results Obtained in the Investigation

I. The Saponification of Fats and Oils by Potassium Hydroxide is a Bimolecular Reaction under the Conditions of this Investigation.

The velocity of saponification of five different oils were determined as follows: Five cubic centimeters of the oil were saponified by 200 c.c. of 2/10 normal amyl alcoholic potassium hydroxide at 25° C. Substitution of the velocity data in the various reaction formulas gave constant values with only the bimolecular reaction formula, therefore the reactions were all bimolecular. See Table I. Two cubic centimeters of methyl acetate were saponified under the same conditions and gave a similar constant. This is a well known bimolecular reaction.

Table 1.[19] Evidence that the Reaction is Bimolecular. The constants in this table were obtained by substituting the experimental data from 5 c.c. oil and 200 c.c. 2/10 normal alkali (amyl alcohol) in the bimolecular reaction formula.

Butter Fat	Cotton Seed	Castor	Olive	Croton	Methyl acetate
.001750	.001529	.001720	.001633	.001789	.005496
1801	1537	1711	1616	1658	5363
1746	1635	1633	1609	1611	5610
1773	1595	1614	1552	1575	5357
1756	1572	1627	1606	1503	5303
1769	1555	1798	1521	1464	5335
1798	1556	1744	1535	1445	
	1579		1768		
Average	1466				
.001770	.001557	.001698	.001605	.001578	.005411

The average saponification value of the oils used is about 200. Therefore, although it would require only 0.91 gram of potassium hydroxide to completely saponify the average oil, there were 2.24 grams of potassium hydroxide present. Inasmuch as Wegscheider states that saponification reactions proceed differenily when the quantity of potassium hydroxide is varied, determinations were made in which five cubic centimeters

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19. The experimental data and method of calculation for each table are given under the corresponding heading at the close of the paper.

of oil were saponified by 200 c.c. of 4/10 normal amyl alcoholic potassium hydroxide. In this case there were 3.57 grams of potassium hydroxide in excess of the 0.91 gram actually required to saponify the 5 c.c. of oil. The results are given in table 2. The reaction proceeds quite rapidly and the results are as nearly constant as could be expected.

Table 2. Evidence that the Reaction is Bimolecular. The constant in this table was obtained by substituting the experimental data from 5 c.c. castor oil and 200 c.c. 4/10 normal amyl alcoholic potassium hydroxide in the bimolecular reaction formula.

Castor oil.
002175
2222
2052
2034
2125
average 002149

When 10 c.c. of castor oil were saponified by 200 c.c. of 2/10 normal amyl alcoholic potassium hydroxide, there was present about 0.42 gram of potassium hydroxide in excess of the amount actually required by the oil. The constant obtained in this case is given in table 3.

Table 3. Evidence that the Reaction is Bimolecular. The constant in this table was obtained by substituting the experimental data from 10 c.c. castor oil and 200 c.c. 2/10 normal amyl alcoholic potassium hydroxide in the bimolecular reaction formula.

Castor oil.

001549

1541

1557

1581

1554

1532

1517

1536

average.001546

The results given in tables 1, 2 and 3 seem to show conclusively that the reactions are bimolecular under the three concentrations investigated. The constants for the glycerides compare favorably with that obtained for methyl acetate which is without a doubt a bimolecular reaction.

II. The Fats and Oils Investigated are all Saponified at approximately the Same Rate.

The data given in table 4 are the average of the constants obtained by saponifying 5 c.c. of the oil or fat in 200 c.c. of 2/10 normal amyl alcoholic potassium hydroxide.

It is evident that butter fat is saponified a little more rapidly than the other four glycerides.

Table 4. The Saponification Constants for Different Oils and Fats under the Same Conditions are approximately the Same.

Butter Fat	Cotton Seed	Croton	Olive	Castor
.001770	.001550	.001578	.001605	.001692

The mean molecular weights of the fatty acids present in the above four vegetable oils are approximately the same. If arranged in the order of their molecular weights it will be seen that the velocity increases with the molecular weight.

Table 5. The Velocity of Saponification Increases with the Molecular Weight of the acid in the Glyceride.

Oil	Cotton Seed	Croton	Olive	Castor
Mol. Wt.	274	279	291	293
Vel. Const.	.001550	.001578	.001605	.001692

The relation indicated in table 5 may or may not be due to a coincidence. It would of course be possible that experimental error was the cause of this apparent relation.

III. The Velocity of Saponification Reactions is Different in Different Solvents.

The evidence supporting this statement was obtained by saponifying Castor oil in three different alcohols. Three different concentrations of oil and potassium hydroxide were

used in each alcohol. The proportions were as follows:

(a) Five cubic centimeters of oil with 200 c.c. of 4/10 normal alcoholic alkali.

(b) Five cubic centimeters of oil with 200 c.c. of 2/10 normal alcoholic alkali.

(c) Ten cubic centimeters of oil with 200 c.c. of 2/10 normal alcoholic alkali.

The constants obtained when using 5 c.c. of oil with 200 c.c. 4/10 normal alcoholic potassium hydroxide are given in table 6.

Table 6. Relative Speed of Saponification of Castor Oil by 4/10 Normal Alkali in Different Alcohols.

	Methyl	Ethyl	Amyl
	.0001079	.001173	.002222
	1051	1135	2034
	1104	1165	2052
	1002	1179	2034
	1010	1214	2125
	1010	1166	
		1205	
Average	.0001020	.001177	.002149
Ratio	1	11.5	21.

When 5 c.c. of oil were saponified by 200 c.c. of 2/10 normal potassium hydroxide, the constants given in table 7 were obtained.

Table 7. Relative Speed of Saponification of Castor Oil by 2/10 Normal Alkali in Different Alcohols.

	Methyl	Ethyl	Amyl
	.00006333	.0008125	.001623
	6384	7865	1605
	6218	7894	1615
	6357	8039	1665
	6244	8044	1645
	6301	8044	1603
			1607
Average	.00006322	.0008002	.001623
Ratio	1	12.6	25.6

When 10 c.c. of oil were saponified by 200 c.c. of 2/10 normal potassium hydroxide the results given in table 8 were obtained.

Table 8. Relative Speed of Saponification of Castor Oil by 2/10 Normal Alkali in Different Alcohols.

	Methyl	Ethyl	Amyl
	.00007046	.0008002	.001549
	7115	8119	1541
	6864	7939	1557
	6958	7987	1581
	7194	7991	1532
	6918	7943	1554
	7074	7968	1517
			1536
Average	.00007023	.0007993	.001546
Ratio	1	11.3	20.1

The average ratio obtained from the above tables is:

1 : 11.8 : 22.2

The reaction is much slower in methyl alcohol than in either of the other alcohols and the ratios obtained are fairly constant. If the constants for ethyl and amyl alcohols are compared, the ratios are more nearly constant as is shown in tables 9, 10 and 11.

Tables 9, 10 and 11. Relative Spped of Saponification of Castor Oil in Different Alcohols.

Table 9. Five Cubic Centimeters of Castor Oil in 4/10 Normal Alkali.

	Ethyl	Amyl
Average Constant	.001177	.002149
Ratio	1	1.83

Table 10. Five cubic centimeters of Castor Oil in 2/10 Normal Alkali.

	Ethyl	Amyl
Average Constant	.0008002	.001623
Ratio	1	2

Table 11. Ten cubic centimeters of Castor Oil in 2/10 Normal Alkali.

	Ethyl	Amyl
Average Constant	.0007993	.001549
Ratio	1	1.9

As a check on the influence of the solvent upon the

velocity of saponification the results obtained by saponifying 2 c.c. of methyl acetate by 200 c.c. of 2/10 normal potassium hydroxide in the different alcohols is given in table 12. If the ratio of the constants in ethyl and amyl alcohol are determined the result is the same as for castor oil. See table 13.

Tables 12 and 13. Relative Speed of Saponification of Methyl Acetate in Different Alcohols.

Table 12.

	Methyl	Ethyl	Amyl
Average Constant	.0001769	.002795	.005339
Ratio	1	15.8	30.1

Table 13.

	Ethyl	Amyl
Average Constant	.002795	.005339
Ratio	1	1.9

From the various data it would seem that the velocity of saponification is about ten times as great in ethyl alcohol as in methyl alcohol and about twice as great in amyl alcohol as in ethyl alcohol. It might therefore be possible to calculate the velocity of any saponification reaction in these alcohols if the velocity of that reaction in one of the alcohols is known. However it would be seen later that the water content of the alcohol is a factor which would have to be considered when calculating a velocity constant.

IV. An Increase of Approximately One per cent in the Amount of Water Present Causes an Increase of about Four Per Cent in the Velocity of Saponification of Castor Oil at 25° C.

The evidence supporting statement IV lies in the results obtained with methyl and ethyl alcohols of different strengths. Only one strength amyl alcohol was used because that alcohol dissolves only a small amount of water. The results for methyl and ethyl alcohol check each other as closely as could be expected. The results are given in tables 14 and 15.

Tables 14 and 15. Relation between the Per Cent Water in the Alcohol and the Speed of Saponification of Castor Oil.

Table 14.

Methyl Alcohol	Constant
92½ % by weight	.0001620
91½ % " "	.0001757

Table 15.

Ethyl Alcohol	Density of Alcohol	Constant
91½ % by weight	.8171	.000952
89½ % by weight	.8238	.001022
87½ % by weight	.8289	.001031
84½ % by weight	.8370	.001298

The data in table 14 show an increase of 4.4 per cent

in the velocity constant for an increase of one per cent in the water content of methyl alcohol. More data were obtained for ethyl alcohol than for methyl. The data in table 15 show an average increase of 3.8 per cent in the velocity constant for every increase of one per cent in the water content of the alcohol.

V. Doubling the Concentration of Alkali Causes an Increase in the Velocity of Reaction but the Increase is not the Same in Alcohols of Different Strengths.

The evidence supporting statement V.was obtained by using two different concentrations of alkali in the three solvents, methyl, ethyl and amyl alcohol. It is evident that the water content of the alcohol is connected with the effect produced by variation in the strength of the alkali.

Table 16. Relation Between the Strength of the Alkali used and the Velocity Constant.

Methyl Alcohol.

Strength of Alcohol	Constant with 2/10 normal Alkali	Constant with 4/10 normal Alkali	Increase in Velocity due to doubling Alkali
95 %	.0000632	.0001020	61.2%
92½%	.0001401	.0001682	20 %
91½%	.0001338	.0001517	13 %

Ethyl Alcohol

Strength of Alcohol	Constant with 2/10 Normal Alkali	Constant with 4/10 Normal Alkali	Increase in Velocity due to doubling Alkali
91 1/2 %	.0008002	.001177	47.1 %
89 1/2 %	.0009487	.001031	7.7 %

Amyl Alcohol (Density .8140)

Constant with 2/10 Normal Alkali	Constant with 4/10 Normal Alkali	Increase in Velocity due to doubling Alkali
.001623	.002149	32.4 %

From the foregoing data it would seem that the stronger the alcohol the greater the acceleration caused by doubling the quantity of alkali. The fact that the velocity is not doubled by doubling the quantity of alkali must be due to the degree of ionization of potassium hydroxide in the alcohol. Therefore it would not be expected that the increase caused by doubling the alkali would be the same in the three solvents because the degree of ionization of potassium hydroxide in the three alcohols is probably quite different.[20]

The effect of increasing the amount of oil gave varying results. It was found as in the case of increasing the amount of alkali that the water content seemed to have some influence on the effect produced by the oil.

Table 17. Relation Between the Amount of Oil Used and the Speed of Saponification.

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20. Jones, Z. f. Phys. Chem. 31, 114, (1899) has shown that the ionization of salts is different in different alcohols.

Methyl Alcohol

Strength of Alcohol.	Constant with 5 c.c. Castor Oil	Constant with 10 c.c. Castor Oil.	Increase in Velocity due to doubling the Oil.
95 %	.00006322	.00007032	11.2 %
92½%	.0001682	.0001809	7.6 %
91½%	.0001517	.0001540	1.5 %

Ethyl Alcohol

Strength of Alcohol.	Constant with 5 c.c. Castor Oil	Constant with 10 c.c. Castor Oil	Change in Velocity due to doubling the Oil.
91½%	.0006002	.0007993	0.11 % Increase
87½	.001049	. 001078	2.7 % Increase

Amyl Alcohol (Density .914 at 16°)

Constant with 5 c.c. Castor Oil	Constant with 10 c.c. Castor Oil	Change in Velocity due to doubling the Oil.
.001623	.001538	5.5% decrease

These results are conflicting but might be explained as follows: In the case of methyl alcohol the velocity constants are very small and therefore the experimental error would be large. On the other hand they follow the same order as in the variation of the amount of alkali. In the case of amyl alcohol the results were carefully checked and there is without a doubt a marked decrease in the velocity when the amount of oil is increased. This fact is possibly due to the formation of considerable glycerol during the reaction, which might cause a decrease in the velocity due to the change in

solvent. It is well known that products of reactions do occasionally influence the velocity of the reaction. The glycerol might increase the velocity in one solvent and decrease it in another solvent.

VI. An Increase of Ten Degrees in the Temperature at Which the Reaction is carried on Cause Castor Oil to be Saponified 2 36 Times as Fast by Ethyl Alcoholic Potassium Hydroxide.

Castor oil was saponified by ethyl alcoholic potassium hydroxide at 15° C.and 25° C., all other factors being exactly the same. The results are given in table 18.

Table 18. Relation Between the Temperature and Speed of Saponification of Castor Oil by Ethyl Alcoholic Potassium Hydroxide.

	Constant At 15° C.	Constant at 25° C.
	.0004527	.001073
	4456	1077
	4538	1056
	4450	1054
	4478	1062
	4479	1018
	4424	1047
	4479	1069
	4386	1066
	4437	1047
	4482	1015
		1013
Average	.0004417	.001053
Ratio	1	2.36

The temperature coefficient, $K\ 25^{\circ} / K\ 15^{\circ}$, for this reaction is 2.36 which is about the average coefficient for ordinary reactions.

VII. The Reaction Does not Go to Completion but only to Equilibrium.

The correctness of statement VII. is easily seen from the difference in the end titrations when oil is saponified by varying amounts of alcoholic potassium hydroxide. The more concentrated the alkali, the further the reaction is carried along. The figures given in table 19 are the number of cubic centimeters of tenth normal potassium hydroxide absorbed by ten cubic centimeters of the reaction mixture.

Table 19. Relation Between the Concentration of Alkali Present in the Solvent and the Amount Used Up at Equilibrium.

Solvent	Cubic centimeters of 2/10 Normal K O H used up by the oil in 10 c.c. of the mixture.	Cubic centimeters of 4/10 Normal K O H used up by the oil in 10 c.c. of the mixture.	Difference
Amyl alcohol	7.64	9.48	1.74
Ethyl "	7.51	9.07	1.56
Methyl "	8.64	10.23	1.59

Summary of Results.

1. The saponification reactions under all conditions described are bimolecular.

2. There is a very small auto catalytic action.

3. The glycerides studied are saponified at approximately the same rate.

4. An increase of 1% in the water content of the alcohol causes an increase of about 4% in the velocity of the reaction.

5. The velocity of saponification of glycerides in amyl alcohol of density .8140 (15.50°) is about twice as great as it is in ethyl alcohol of density .8171 (15.50°) and about ten times as great in this ethyl alcohol as it is in methyl alcohol of density .8100 (15.50°).

6. The temperature coefficient of the reaction $k_{25°}/k_{15°}$ is 2.36 in the case where castor oil is saponified in ethyl alcohol.

7. The velocity is greatly accelerated by increasing the amount of alkali but no definite ratios could be determined from the data.

8. When amyl alcohol of a density .8140 is used as the solvent, an increase in the amount of oil causes a decrease in the velocity of reaction. While in the case of methyl and ethyl alcohols there seems to be an increase in the velocity due to the increase in amount of oil.

Experimental Data and Calculations

As described above, in carrying out a determination, the oil dissolved in the solvent, is mixed with the alkali dissolved in the solvent. At intervals, the volume of 1/10 normal alkali remaining in 10 c.c. of the mixture is determined as follows:

Ten cubic centimeters of the mixture is run into excess, either 20 c.c. or 40 c.c. of 1/10 normal H Cl. The excess acid is then titrated with 1/10 normal Ba $(OH)_2$. The difference between the volume of 1/10 normal H Cl used and 1/10 normal Ba $(OH)_2$ used gives the volume of 1/10 normal alkali present in 10 c.c. of the mixture. This value is given in the second column in the experimental tables below.

The second order reaction formula used in all of the calculations is:

$$K = \frac{2.3025}{T_e\ t} \log \frac{T_t\ (T_0 - T_e)}{T_0\ (T_t - T_e)}$$

K = Velocity constant.

T_0= Volume of 1/10 normal alkali present in 10 c.c. of the mixture at first titration.

T_e= Volume of 1/10 normal alkali present in 10 c.c. of the mixture at the end of the reaction.

T_t= Volume of 1/10 normal alkali present in 10 c.c. of the mixture at time t.

t = Time in minutes after the first titration.

In the experimental data below T_o is the first value and T_e the lost value under the second column.

Data[21] For Table 1.

Five cubic centimeters of fat or oil was saponified by 200 c.c. of 2/10 normal amyl alcoholic potassium hydroxide at 25° C.

Butter Fat			Cottonseed Oil		
t	T_t	K	t	T_t	K
0	17.42		0	17.52	
12	15.19	.001750	9	16.14	.001529
20	14.11	1801	16	15.31	1537
29	13.31	1746	23	14.52	1635
40	12.48	1773	31	13.95	1595
49	12.01	1756	41	13.37	1572
56	11.68	1769	51	12.92	1555
71	11.13	1798	62	12.51	1556
E	9.70		72	12.36	1579
			87	11.98	1466
			E	10.83	

21. The Experimental data on Castor Oil were lost after the result had been tabulated. Another determination of the same is given in table 7.

Olive Oil			Croton Oil		
t	T_t	K	t	T_t	K
0	2.39		0	17.50	
19	4.66	.001633	11	15.82	.001789
27	5.28	1616	19	15.03	1658
36	5.81	1609	26	14.47	1611
44	6.13	1552	36	13.83	1575
52	6.51	1606	46	13.40	1503
62	6.73	1521			
71	6.98	1535	55	13.13	1464
78	7.36	1768	65	12.76	1445
E	8.15		E	11.08	

Methyl Acetate. Two cubic centimeters in 200 c.c. of 2/10 normal amyl alcoholic potassium hydroxide at 25° C.

t	T_t	K
0	16.68	
6	14.55	.005496
12	13.42	5363
18	12.64	5610
23	12.33	5357
30	11.98	5335
36	11.79	5303
E	11.36	

Data For Table 2

Five cubic centimeters of castor oil saponified by 200 c.c. 4/10 normal amyl alcoholic K O H at 25° C.

t	T_t	K
0	35.73	
1	35.28	.002175
4.5	34.18	2222
8	33.49	2034
11.5	32.85	2052
15.	32.38	2034
18.5	31.92	2125
E	30.52	

Data For Table 3

Ten cubic centimeters of Castor Oil saponified by 200 c.c. of 2/10 normal amyl alcoholic potassium hydroxide at 25° C.

t	T_t	K
0	17.28	
5	15.89	.001549
11	14.55	1541
15	13.78	1557
20	12.93	1581
25	12.34	1532
32	11.49	1554
40	10.82	1517
50	10.02	1536
E	5.65	

Data for Table 6.

Five cubic centimeters of castor oil saponified by 200 c.c. 4/10 normal alcoholic potassium hydroxide at 25°C., in the three alcohols, methyl, ethyl and amyl. The data for amyl alcohol are the same as given in table 2.

Methyl alcohol			Ethyl alcohol		
t	T_t	K	t	T_t	K
0	36.92		0	36.12	
19.5	36.39	.0001079	4.5	35.23	.001173
26.5	36.23	1051	7.5	34.77	1135
33.5	36.11	1104	11.	34.24	1165
51.5	35.70	1002	14.	33.85	1179
63.5	35.44	1010	17.	33.47	1214
73.5	35.24	1010	20.5	33.21	1166
End	29.77		24.	32.86	1205
			End	30.93	

Data for Table 7.

Five cubic centimeters of castor oil saponified by 200 c.c. 2/10 normal alcoholic potassium hydroxide at 25° C, in the three alcohols, methyl, ethyl and amyl.

Methyl Alcohol			Ethyl Alcohol		
t	T_t	K	t	T_t	K
0	18.94		0	18.68	
8	18.07	.00006333	17	17.32	.0008125
20	18.76	6384	23	16.96	7865
59	18.43	6218	32	16.47	7894
117	17.97	6357	42	15.96	8039
146	17.76	6244	54	15.47	8044
211	17.32	6301	68	15.00	8044
End	11.36		End	12.49	

Amyl Alcohol		
t	Tt	K
0	18.10	
10	16.70	.001623
14	16.28	1605
18	15.89	1615
23	15.42	1665
33	14.79	1643
41	14.42	1603
52	13.96	1607
End	12.40	

Data for Table 8.

Ten cubic centimeters of castor oil saponified by 200 c.c. 2/10 normal alcoholic potassium hydroxide at 25° C. in the three alcohols, methyl, ethyl and amyl.[22]

	Methyl Alcohol			Ethyl Alcohol	
t	T_t	K	t	T_t	K
0	18.85		0	17.30	
46	18.01	.00007046	15	15.10	.0008002
59	17.79	7115	27	13.72	8119
74	17.58	6864	33	13.23	7939
89	17.30	6958	39	12.70	7987
119	16.85	7194	45	12.24	7991
172	16.18	6918	52	11.78	7943
188	15.95	7074	59	11.33	7968
End	4.76		End	4.79	

22. Data for Amyl Alcohol same as table 3.

Data for Tables 12 and 13.

Two cubic centimeters of methyl acetate saponified by 200 c.c. of 2/10 normal alcoholic potassium hydroxide at 25°C, in the three alcohols, methyl, ethyl and amyl.[23]

Methyl Alcohol			Ethyl Alcohol		
t	T_t	K	t	T_t	K
0	18.48		0	18.14	
15	18.09	.0001841	8.5	15.92	.002800
33	17.69	1766	15.	14.77	2808
41.5	17.51	1755	18.	14.39	2786
47.5	17.21	1693	22.5	13.92	2753
55	17.20	1806	33.	13.10	2734
64	17.04	1773	End	11.33	
73	16.89	1752			
End	10.59				

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23. Data for Amyl Alcohol same as Table 1.

Data for Table 18

Five cubic centimeters of castor oil saponified by 200 c.c. 2/10 normal ethyl alcoholic K O H at 25° C and 15°C (Alcohol was 87½%)

Constant at 15° C			Constant at 25° C		
t	T_t	K	t	T_t	K
0	19.18		0	18.66	
21.9	18.00	.0004527	8.7	17.66	.001073
32.6	17.54	4456	14.7	17.08	1077
41.3	17.16	4538	22.2	16.50	1056
51.7	16.81	4450	29.7	15.99	1054
62.8	16.43	4479	36.5	15.57	1062
75.55	16.05	4478	45	15.23	1018
85.2	15.82	4424	63	14.46	1047
95.4	15.54	4479	70.5	14.18	1069
107.8	15.31	4386	84.2	13.82	1069
121.4	15.01	4437	92.2	13.65	1066
148.6	14.52	4482	100.7	13.52	1047
End	12.15		109.2	13.43	1015
			117.7	13.27	1034
			End	12.24	

It was thought unnecessary to give any data for tables 14 to 17 except that included in the tables.

This work was undertaken at the suggestion and under the direction of Dr. Ernest Anderson.